(19) World Intellectual Property Organization International Bureau



T MANTE SAN COMPANION DE COMPANION DE LA COMPANION DE COMPANION DE COMPANION DE COMPANION DE COMPANION DE COMP

(43) International Publication Date 20 June 2002 (20.06.2002)

PCT

(10) International Publication Number WO 02/49136 A2

(51) International Patent Classification7: 8/10, 8/24

H01M 8/04,

PCT/US01/46948

(74) Agent: KOCH, WILLIAM, E., Corporate Law Department, Intellectual Property Section, 3102 North 56th Street, MD: AZ11/56-238, Phoenix, AZ 85018 (US).

- 8/10, 8/24
 (21) International Application Number:
- (22) International Filing Date: 5 December 2001 (05.12.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/738,131

15 December 2000 (15.12.2000) U

- (71) Applicant: MOTOROLA, INC., A CORPORATION OF THE STATE OF DELAWARE [US/US]; 1303 East Algonquin Road, Schaumburg, IL 60196 (US).
- (72) Inventors: NEUTZLER, Jay.; 2500 Sawmill Road, Apt. 912, Santa Fe, NM 87505 (US). BOSTAPH, Joseph, W.; 2052 East Folley Street, Chandler, AZ 85225 (US). FISHER, Allison, M.; 21433 South 140th Street, Chandler, AZ 85249 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,

SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA,

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,

Published:

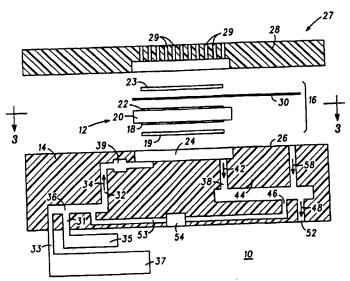
NE, SN, TD, TG).

ZW.

without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: DIRECT METHANOL FUEL CELL INCLUDING A WATER MANAGEMENT SYSTEM



(57) Abstract: A fuel cell device (10) and method of forming the fuel cell device including a base portion (14), formed of a singular body, and having a major surface (26). At least one fuel cell membrane electrode assembly (16) including a plurality of hydrophilic threads (30) for the wicking of reaction water is formed on the major surface of the base portion. A fluid supply channel (32) including a mixing chamber (36) is defined in the base portion and communicating with the fuel cell membrane electrode assembly for supplying a fuel-bearing fluid (34) to the membrane electrode assembly. An exhaust channel (38) including a water recovery and recirculation channel (53) is defined in the base portion and communicating with the membrane electrode assembly and the plurality of hydrophilic threads. The membrane electrode assembly and the cooperating fluid supply channel and cooperating exhaust channel forming a single fuel cell assembly.

0 02/49136

PCT/US01/46948 WO 02/49136

DIRECT METHANOL FUEL CELL INCLUDING A WATER MANAGEMENT SYSTEM

Field of Invention

5

10

The present invention pertains to fuel cells, and more particularly to a direct methanol fuel cell including a water management system and a method of fabricating the system, in which water is collected and redistributed during the process of generating electrical energy.

Background of the Invention

15

20

"battery are general, Fuel cells in replacements", and like batteries, produce electricity through an electrochemical process without combustion. The electrochemical process utilized provides for the combining of protons with oxygen from air or as a pure The process is accomplished utilizing a proton exchange membrane (PEM) sandwiched between two electrodes, namely an anode and a cathode. Fuel as known, are a perpetual provider cells, electricity. Hydrogen is typically used as the fuel for producing the electricity and can be processed from methanol, natural gas, petroleum, or stored as Direct methanol fuel cells (DMFCs) pure hydrogen. 30

3

top of another. Conventional fuel cells can also be stacked in parallel (positive to positive) to obtain higher power, but generally larger fuel cells are simply used instead.

During operation of a direct methanol fuel cell, 5 a dilute aqueous methanol (usually 3-4% methanol) solution is used as the fuel on the anode side. the methanol concentration is too high, then there is a methanol crossover problem that will reduce the efficiency of the fuel cell. If the methanol concentration is too low then there will not be enough fuel on the anode side for the fuel cell reaction to take place. Current DMFC designs are for larger stacks with forced airflow. The smaller air breathing DMFC designs are difficult to accomplish because of 15 complexity in miniaturizing the system portable applications. Carrying the fuel in the form of a very dilute methanol mixture would require carrying a large quantity of fuel which is not practical for the design of a miniature power source 20 for portable applications. Miniaturizing the DMFC system requires having on hand separate sources of methanol and water and mixing them in-situ for the fuel cell reaction. To aid in supplying methanol and 25 water to the anode, it would be beneficial recirculate the aqueous fuel mixture after the fuel cell reaction, and recycle the water generated at the cathode in the fuel cell reaction, as well as the

5

The above problems and others are at partially solved and the above purposes and others are realized in a fuel cell device and method of forming the fuel cell device including a base portion, formed of a singular body, and having a major surface. At least one membrane electrode assembly is formed on the major surface of the base portion. The membrane electrode assembly includes hydrophilic properties for the water management of by-product water. A fluid supply channel is defined in the base portion and communicates with the at least one membrane electrode assembly for supplying a fuel-bearing fluid to the at least one membrane electrode assembly. An exhaust channel is defined in the base portion communicating with the at least one membrane electrode assembly. The exhaust channel is spaced apart from the fluid supply channel for exhausting by-product fluid, including water, from the at least one membrane electrode assembly. The membrane electrode assembly cooperating fluid supply channel and the and cooperating exhaust channel form a single fuel cell assembly.

10

15

20

25 <u>Brief Description of the Drawings</u>

Referring to the drawings:

In the prior art, liquid water current dependant. removal is largely done through temperature gradient (2-phase), hydrophobic treatments, micro/macro porous diffusion backings, and convective flow. Ιt 5 disclosed in the present invention to provide for water management of a fuel cell device that includes a means for water management including a hydrophilic material, more particularly hydrophilic threads to well as membrane, as hydrate the evenly remove/redirect liquid water accumulation from the 10 side of the fuel cell device. cathode accumulation, the water is fed back to the anode side of the fuel cell device for reaction and dilution of the methanol stream.

Turning now to the drawings, FIG. 1 illustrates 15 in simplified sectional view a direct methanol fuel cell including a water management system fabricated according to the present invention. Illustrated is a fuel cell system, generally referenced 10, including a single fuel cell assembly 12. Fuel cell 12 is formed 20 on a base portion. Base portion 14 is designed to be impermeable to the mixture of fuel and oxidizer materials that is utilized to power fuel cell 12. Typically a hydrogen-containing fuel/oxidizer mixture is utilized to power fuel cell 12. Suitable fuels that 25 are consumed by fuel cell 12 to produce electrical energy are hydrogen-containing materials such hydrogen, methane and methanol. In this particular

PCT/US01/46948 WO 02/49136

to 98%). The fuel cell assembly 10 would also be able to use other fuels, such as hydrogen or ethanol, but it should be noted that ethanol is not efficient, nor does it produce as much power as does 5 the use of methanol. In this particular example a separate methanol tank 35 and water tank 37 are utilized to supply the fuel-bearing fluid 34. methanol will be pumped in at a given rate, and the water will be added as needed determined by the efficiency of the integrated water management system (discussed presently), which is monitored by a 39. methanol concentration sensor concentration sensor 39 helps maintain the methanol ratio in the mixture. The methanol and water will be homogeneously mixed in mixing chamber 36 before flowing to fuel cell 12.

In addition, there is formed in base portion 14, an exhaust channel 38 communicating with fuel cell 12. Exhaust channel 38 serves to remove exhaust products 42 from fuel cell 12, namely carbon dioxide and a 20 water/methanol mixture. During operation, exhaust products are separated in a carbon dioxide separation chamber 44 into the water/methanol mixture 46 and a carbon dioxide gas 48. Next, gas 48 is expelled through an exhaust outlet 52, such as a gas permeable 25 membrane and water/methanol mixture 46 is recirculated through a recirculating channel 53, having included as a part thereof a pump 54, such as a MEMs-type pump, or

10

11

molybdenum, and alloys of platinum, palladium, gold, nickel, tungsten carbide, molybdenum, and ruthenium. Film 20 is further described as formed of a Nafion® type material that prevents the permeation of fuel from the anode side (first electrode 18) to the cathode side (second electrode 22) of fuel cell 12.

5

10

15

20

Membrane electrode assembly 16 in this particular example is positioned in a recess 24 formed in an uppermost major surface 26 of a base portion 14. It is anticipated by this disclosure that membrane electrode assembly 16 can be positioned on major surface 26 of base portion 14 without the need for the formation of recess 24. In this instance, a spacer (not shown) would be utilized to avoid complete compression of membrane electrode assembly 16.

Planar stack array 10 further includes a top portion, more specifically, in this particular embodiment, a current collector 28, including a plurality of air flow-throughs 29 positioned to overlay membrane electrode assembly 16. Current collector 28 is formed as part of a cap portion, generally referenced 27. Cap portion 27 provides for the exposure of second electrode 22 to ambient air.

During fabrication, fuel cell membrane electrode

25 assembly 16 is formed using a hot press method, or
other standard method known in the art. More
particularly, first electrode 18 is formed or
positioned in contact with base portion 14. Various

13

cell membrane electrode assembly 16 is comprised of first electrode 18, film 20, second electrode 22, and gas diffusion media layers, or more particularly carbon cloth backing layers, 19 and 23.

5 Positioned on an uppermost surface of second electrode 22, therefore sandwiched between electrode 22 and carbon cloth backing 23, plurality of hydrophilic threads 30. Hydrophilic threads 30 are preferably located between electrode 22 10 and carbon cloth backing 23 to provide for even hydration of fuel cell membrane electrode assembly 16, and more particularly film 20. Hydrophobic threads 30 are disclosed in this embodiment as comprised of a polyester fiber material, but it should be understood 15 that additional hydrophilic fibers are anticipated by this disclosure. The hydrophobicity of carbon backing layer 23 provides for hydrostatic pressure to "push" the water along hydrophilic threads 30. Subsequent to accumulation of the water in hydrophilic threads 30, the water is fed back to the anode side of fuel cell 20 through water recovery return channel reaction and dilution of the methanol stream. Hydrophilic threads 30 are positioned parallel to flow channels (not shown) between second electrode 25 (cathode electrode) and carbon backing layer 23, gas diffusion backing layer. Hydrophilic threads 30 provide for the wicking away of water prior to its reaching carbon backing layer 23.

15

electrode 22, thus connected in parallel electrical interface.

Referring now to FIG. 2, illustrated is a fuel cell array, generally referenced 10'. It should be noted first embodiment of the all components illustrated in FIG. 1, that are similar to components of this particular embodiment as illustrated in FIG. 2, are designated with similar numbers, having a prime added to indicate the different embodiment. Fuel cell array 10' has formed as a part thereof, four individual 10 fuel cells 12', having an overall base portion 14' dimension of approximately 5.5cm x 5.5cm x .5cm, and individual fuel cell 12' area of $4 \times 1.5-2.0$ cm squares. Each individual fuel cell 12' is capable of generating approximately 0.5V and 22.5mA/cm of power. Fuel cells 15 12' are formed on a base portion 14, each fuel cell 12' being spaced at least 1mm apart from an adjacent fuel cell 12'. It should be understood that dependent upon the required power output, any number of fuel cells 12' can be fabricated to form a planar array of fuel 20 cells, from one fuel cell as illustrated in FIG. 1, to numerous fuel cells.

Similar to fuel cell system 10, described with respect to FIG. 1, fuel cell system 10' includes a base portion 14', designed to be impermeable to the mixture of fuel and oxidizer materials that is utilized to

methanol in water (99.5%-96.0%). Similar to FIG. 1, in this particular example a separate methanol tank 35' and water tank 37' are utilized to supply the fuel-bearing fluid 34. The methanol will be pumped in at a given rate, and the water will be added as needed determined by the efficiency of the integrated water management system (discussed presently), which is monitored by a methanol concentration sensor 39'. Methanol concentration sensor 39' helps maintain the methanol ratio in the mixture. The methanol and water will be homogeneously mixed in mixing chamber 36' before flowing to fuel cells 12'.

10

In addition, there is formed in base portion 14', an exhaust channel 38' communicating with fuel cells Exhaust channel 38' serves to remove exhaust 12'. 15 products 42' from fuel cell 12', namely carbon dioxide During operation, and a water/methanol mixture. exhaust products are separated in a carbon dioxide separation chamber 44' into the water/methanol mixture 46' and a carbon dioxide gas 48'. Next, gas 48' is 20 expelled through an exhaust outlet 52', such as a gas permeable membrane and water/methanol mixture 46' is recirculated through a recirculating channel 53', having included as a part thereof a pump 54', such as a MEMs-type pump, or check valve type assembly, back to 25

19

is further described as formed of a Nafion® type material that prevents the permeation of fuel from the anode side (first electrode 18') to the cathode side (second electrode 22') of fuel cells 12'.

Membrane electrode assemblies 16' in this particular example are positioned in a plurality of recesses 24' formed in an uppermost major surface 26' of a base portion 14. It is anticipated by this disclosure that membrane electrode assemblies 16' can be positioned on major surface 26' of base portion 14' without the need for the formation of recesses 24'.

5

10

15

20

Planar stack array 10' further includes a top portion, more specifically, in this particular embodiment, a current collector 28' positioned to overlay membrane electrode assembly 16'.

During fabrication, fuel cell membrane electrode assemblies 16' are formed using a hot press method, or other standard method known in the art. More particularly, first electrode 18' is formed or positioned in contact with base portion 14'. Various materials are suitable for the formation of electrode 18'.

In this specific embodiment, and for exemplary purposes, first electrode 18' has a dimension of

21

fuel cells 12' through water recovery return channel 58' for reaction and dilution of the methanol stream 30'. Hydrophilic threads 30' are positioned parallel to flow channels (not shown) on an uppermost surface of carbon backing layer 23', or gas diffusion backing layer. Hydrophilic threads 30' provide for the wicking away of water prior to its reaching a current collector 28' (discussed presently).

Finally, current collector 28' is positioned 10 relative to second electrode 22'. Current collector 28' formed at least 0.1mm thick and of a length dependent upon a point of contact on fuel cells 12'. In the alternative, fuel cells 12' can be electrically interfaced using silver conducting paint deposited by evaporation or sputtering. Materials suitable for 15 this are gold (Au), silver (Au), copper (Cu), or any other low electrical resistant material. The bulk resistivity of the electrode material and area of the electrode will dictate the type of current collection scheme to minimize ohmic losses. 20 In addition, anticipated by this disclosure to achieve electrical interface between fuel cells 12', are patterned conductive epoxy and pressing, wire bonding, bonding, spring contacts, flex tape, or alligator 25 clips.

ratio of methanol to water. Once properly mixed, the fuel-bearing fluid flows through the fluid supply channel toward the fuel cell 12. An optional MEMstype pump 40 is utilized to assist with this flow. Concentration sensors 39 are provided to assist with monitoring the methanol concentration, and temperature of the fuel-bearing fluid. The fuelbearing fluid next reaches fuel cell stack 12 and generates power. The power is supplied to a DC-DC converter 62 which converts the generated voltage to a 10 useable voltage for powering a portable electronic device, such as a cell phone 60 and included as a part thereof a rechargeable battery 64. During operation spent fluid is exhausted through the exhaust channel toward a carbon dioxide separation chamber and carbon 15 dioxide vent, generally referenced 44. In addition, water is recovered from the cathode side of the fuel cell 12 by hydrophilic threads 30, and from the separation chamber 44 and is recirculated through a recirculating channel back to the mixing chamber 36. recirculating of fluid provides for consumption of less water from water tank 37 and thus less replenishment of water tank 37.

Accordingly, disclosed is a fuel cell system including a water management system and method of 25 fabrication which provides for the fabrication of the system, providing for inclusion of a single fuel cell or a plurality of fuel cells to be formed on a planar

10

15

What is claimed is:

- A fuel cell device comprising:
- a base portion, formed of a singular body, and
 5 having a major surface;
 - at least one fuel cell membrane electrode assembly formed on the major surface of the base portion, the at least one fuel cell membrane electrode assembly including a plurality of hydrophilic threads positioned to absorb reaction water;
 - a fluid supply channel defined in the base portion and communicating with the at least one fuel cell membrane electrode assembly, the fluid supply channel including a mixing chamber and at least one fuel-bearing fluid inlet;

an exhaust channel defined in the base portion and communicating with the at least one fuel cell membrane electrode assembly, the exhaust channel including a water recovery and recirculation channel in communication with the plurality of hydrophilic threads, the exhaust channel spaced apart from the fluid supply channel for exhausting fluid from the at least one fuel cell membrane electrode assembly, the at least one fuel cell membrane electrode assembly and the cooperating fluid supply channel and cooperating exhaust channel forming a single fuel cell assembly;

- 5. A fuel cell device as claimed in claim 4 wherein the fuel cell membrane electrode assembly further includes a carbon cloth backing positioned on the first electrode on a side opposite the adjacent film, and a carbon cloth backing positioned on the second electrode on a side opposite the adjacent film.
- 6. A fuel cell device as claimed in claim 5 wherein the plurality of hydrophilic threads positioned on an uppermost surface of the second electrode, characterized as sandwiched between the second electrode and the carbon cloth backing, plurality of hydrophilic threads spaced apart parallel to one another.

- A fuel cell device as claimed in claim 4 7. wherein the first and second electrodes comprise a material selected from the group consisting of platinum, palladium, gold, nickel, tungsten carbide, 20 ruthenium, molybdenum, and alloys οf platinum, palladium, gold, nickel, tungsten carbide, molybdenum, and ruthenium.
- A fuel cell device as claimed in claim 5 8. 25 wherein film overlying the the first electrode comprises of a proton exchange type material.

29

spaced apart from the fluid supply channel for exhausting fluid from the at least one spaced apart fuel cell membrane electrode assembly, the exhaust channel further including a water recovery and recirculation channel in fluidic communication with the at least one fuel cell membrane electrode assembly, in combination the at least one fuel cell membrane electrode assembly and the cooperating fluid supply channel and cooperating exhaust channel forming a single fuel cell assembly; and

a top portion including a plurality of electrical components for electrical integration of the plurality of formed fuel cell assemblies.

15 11. A method of fabricating a fuel cell device comprising the steps of:

providing a base portion formed of a material selected from the group consisting of ceramic, plastic, glass, and silicon;

- forming a fluid supply channel in the base portion for supplying a fuel-bearing fluid to at least one fuel cell membrane electrode assembly, the fluid supply channel further including a mixing chamber and a methanol concentration sensor;
- forming an exhaust channel in the base portion, the exhaust channel spaced apart from the fluid supply channel for exhausting fluid from the at least one spaced apart fuel cell membrane electrode assembly,

SUCCIO MO OSAGESEAS I -

5

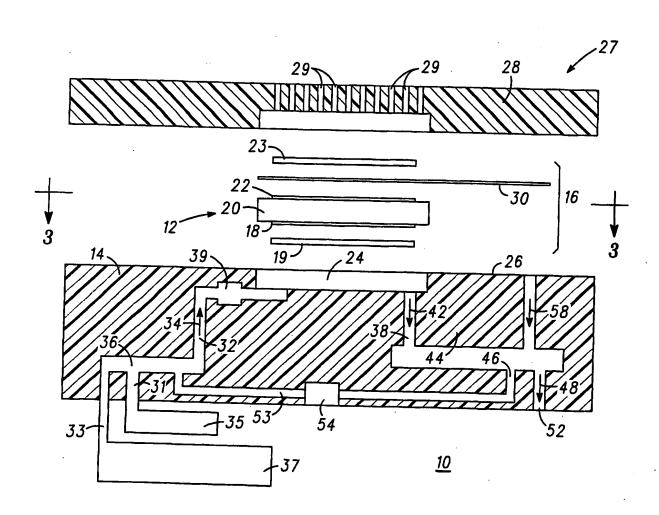


FIG. 1

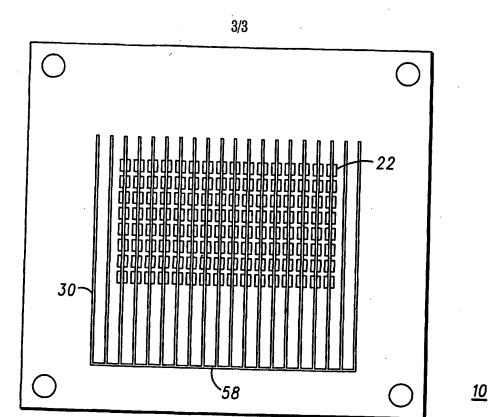


FIG.3

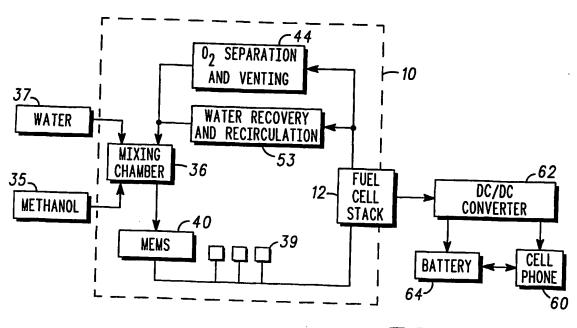


FIG. 4